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(54) Method for producing raw materials for a reformer by cracking and desulfurizing petroleum fuels.

(57) The present invention provides a method for producing raw materials for a reformer by cracking and desulfurizing petroleum fuels, characterized by cracking and desulfurizing petroleum fuels in a desulfurizer in the fuel cell electricity generation process at a temperature of 300-600°C, preferably 350-500°C, a pressure of 1-10 kg/cm^2, an H_2/oil of 500-2000, preferably 800-1000, and an SV of 0.5-4 hr^{-1} using a zeolite catalyst such as Y-type zeolite or a metallosilicate catalyst such as one having an Si/Me atomic ratio of 40-3200 where Me is Al, Ni, Co, Mo, W, Fe, Cr or Ga.

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METHOD FOR PRODUCING RAW MATERIALS FOR A REFORMER BY CRACKING AND DESULFURIZING PETROLEUM FUELS

The present invention relates to an improvement in desulfurization step in fuel cell electricity generation process which uses petroleum products as raw material fuels and aims at diversification of source fuels.

Fuel cell electricity generation process is one of future type energy conversion techniques which have many features such as saving of energy and less environmental pollution. Fuels for fuel cell are produced mainly from natural gas and methanol, but can also be produced from liquid fuels such as petroleum. However, according to steam reforming method, up to butane fraction can be practically obtained in large-scale plant, but this is still insufficient from a standpoint of fuel cell electricity generation process which uses petroleums.

A representative flow sheet of electricity generation process by fuel cells using petroleums is shown in Figs.1 and 2.

In combination of desulfurizer and reformer in the above process, load of catalyst for the reformer increases with the raw materials becoming heavier. Therefore, load for reforming catalyst is reduced by allowing catalyst in desulfurizer to have cracking function, and thus, raw material fuels can be diversified.

The present invention relates to a method for obtaining raw materials for the reformer by cracking and desulfurizing petroleum fuels, characterized by cracking and desulfurizing petroleum fuels in a desulfurizer in the electricity generation process by fuel cell at a temperature of 300-600°C, preferably 350-500°C, a pressure of 1-10 kg/cm^2, an H_2/oil ratio of 500-2000, preferably 800-1000, and an SV of 0.5-4 hr^{-1} using a zeolite catalyst such as Y-type zeolite or matallosilicate catalyst (Si/Me atomic ratio : 40-3200, where Me is Al, Ni, Co, Mo, W, Fe, Cr or Ga).

Fig. 1 is a flow sheet of a fuel cell process.

Fig. 2 is another flow sheet of a fuel cell process.

Fig. 3 is a flow sheet of preparation of metallosilicate catalyst of the present invention.

Fig. 4 is a graph which shows relation between reaction temperature of the present invention and cracking rate.

In Figs. 1 and 2 which are flow sheets of fuel cell electricity generation processes to which the present invention is applied, the reference numbers indicate the following :

1 : desulfurizer, 2 : adsorber, 3 : reformer provided with a furnace, 4 : shift converter (4-A : low-temperature shift converter, 4-B : high-temperature shift converter, 5 : fuel cell, 6 : seperation membrane.

Kerosene, naphtha, LPG, and the like are used as raw material fuels for fuel cells.

In the desulfurizer, Y-type zeolite or metallosilicate catalyst (Si/Me atomic ratio : 40-3200, where Me is Al, Ni, Co, Mo, W, Fe, Cr or Ga) is used as desulfurizing catalyst having cracking function.

Reaction conditions in desulfurizer are selected so that sulfur content in product is at most 1 ppm taking into consideration the poisoning of reforming catalyst and cracking rate of the raw material fuel is 10-70%.

Cracking rate here means a proportion of components in the product lighter than raw material. In the adsorber, sulfur contained in the raw material fuel is removed in the form of hydrogren sulfide.

In the reformer, the raw material are converted to a product-gas comprising hydrogen as main component and CO and CO_2 in accordance with the following reaction formula.

$$C_3H_8 + 4H_2O = 2CO + CO_2 + 8H_2$$

Catalysts used are commercially available noble metal or nickel-supporting alumina catalysts.

Composition-range of raw material which can be applied to reformer is specific gravity : 0.5-0.85, components : C_3-C_{20} hydrocarbons.

Conditions in the reformer are temperature :

700-800°C ; pressure : 10 kg/cm^2 or less ; H_2O/C (molar ratio) : at least 2 ; and SV : 0.5-4.0 hr^{-1}.

Compositions of the product-gas in the reformer is typically H_2 65-80 vol%, CO 5-20 vol%, and CO_2 5-25 vol%, but this is may vary depending on operation-conditions.

The upper and lower limit of the above ranges are determined by changing operation-conditions of reformer, but operation-conditions by which content of H_2 is close to the upper limit are preferred.

One example of composition of product-gas from th reformer when kerosene, naphtha and LPG are used as raw material is shown in Tabl 1.

Table 1

Gas	Raw material kerosene (vol%)	Raw material naphtha (vol%)	Raw material LPG (vol%)
H	72.0	73.9	74.2
CO	10.8	10.0	9.7
CO_2	17.2	16.1	16.1

In shift converter, reaction is carried out in the presence of H_2O according to the following reaction formula.

$$CO + H_2O = CO_2 + H_2$$

In the shift converter, Fe-based catalysts and Cubased catalysts are used and there are the two reactions of high-temperature shift reaction and low-temperature shift reaction depending on catalyst used.

The high-temperature shift reaction is carried out at a temperature of 330°C or higher and a pressure of 1-35 kg/cm^2 and the low-temperature shift reaction is carried out at a temperature of 190-370°C and at a pressure of 1-30 kg/cm^2.

Generally, both high-temperature shift converter and low-temperature shift converter are necessary for reducing the CO concentration in converted gas to 1 vol% or less.

In the fuel cell electricity generation process as shown in Fig.2, a polyimide type gas separation membrane is used in place of shift converter. In this case, reformed gas is treated under the conditions of temp rature 50-150°C and pressure 2-10 kg/cm^2, and CO in the reformed gas is mostly separated and removed.

Example

The following five metallosilicate catalysts were used as cracking and desulfurizing catalysts.

Catalyst A : Al-silicate (Si/Al = 40)
Catalyst B : Ni-silicate (Si/Ni = 40)
Catalyst C : Co ion exchanged type Al-silicate (Si/Al = 40)
Catalyst D : Al-silicate (Si/Al = 3200)
Catalyst E : Fe-silicate (Si/Fe = 3200)
Properties of the above catalysts are shown in Table 2.

Table 2

Catalyst	A	B	C	D	E
Surface area (m^2/g)	382.9	352.8	315.6	309.9	372.3
Pore volume (ml/g)	0.29	0.20	0.28	0.18	0.26

Preparation method of metallosilicate catalyst is shown in Fig.3. Hydrothermal synthesis of metallosilicate catalyst was carried out in an autoclave using water-soluble salts of active metals such as sulfate, nitrate and chloride at 100-250°C, drying was carried out at 120°C for 4 hours, and calcination was carried out at 540°C for 3.5 hours. Then, sodium ion of the metallosilicate was ion exchanged with ammonium ion and th metallosilicate was dried and calcined at 540°C and then was used.

Desufurization reaction was carried out using a pressure flowing type reactor with a reaction tube made of SUS316 and having an inner diameter f 16 mm and a length of 660 mm.

120 ml of the catalyst (8-16 meshes) was packed and 70 ml thereof, i.e., from the center of the upper electric furnace to the center of the lower electric furnace was made as effective catalyst packing amount.

Kerosen and naphtha w re used as raw materials for desulfurization. For k rosene, reaction was carried out under the conditions of pressure 6 kg/cm^2, SV 1 hr^{-1} and H_2/oil ratio 1000 at temperatures of 400°C and 500°C.

The results for liquid product are shown in Table 3 on kerosene and in Table 5 on naphtha. Furthermore, results on the whole products including gas component for kerosene are shown in Table 4.

Analysis of cracking products (liquid component) of keresene and naphtha was carried out using SHIMADZU GC-9A (column CBP.1-M50) and analysis of cracking products (gas component) was carried out using SHIMADZU GC-9A (column : sebaconitrile).

Table 3

	Reaction temperature (°C)	Composition of product		
		C_9 and lower (wt%)	C_{10-12} (wt%)	C_{13} and higher (wt%)
Raw material kerosene	-	5.9	55.1	39.0
Catalyst A	400	35.4	35.5	29.1
Catalyst A	500	56.6	28.8	14.6
Catalyst B	400	22.6	42.2	35.2

Table 4

	Reaction temperature (°C)	Composition of product		
		C_5 and lower (wt%)	C_{6-9} (wt%)	C_{10} and higher (wt%)
Raw material kerosene	-	0	5.9	94.1
Catalyst A	400	29.4	27.9	42.7
Catalyst A	500	36.9	25.8	37.3

Table 5

Catalyst	Reaction conditions			Reaction products (wt%)			
	Temp. (°C)	SV (hr^{-1})	Pressure (kg/cm^2)	C_6 and lower	C_7-C_9	C_{10} and higher	Aromatics (BTX)
Raw material naphtha				0.4	74.3	10.5	14.8
A	400	0.8	6	61.4	13.2	5.9	19.5
A	500	0.8	6	58.3	8.5	6.1	27.1
A	500	1.3	25	48.1	6.7	6.4	38.8
A	400	1.9	6	55.2	12.3	9.5	23.0
D	500	2.0	6	53.7	24.0	5.7	16.6
D	500	0.9	6	56.1	21.9	6.8	15.2
E	500	1.9	6	54.4	22.3	6.2	17.1
E	500	0.9	6	46.7	24.1	9.2	20.0

Furthermore, for kerosene, relation between reaction temperature and cracking rate was examined at temperatures of 400°C, 450°C and 500°C, a pressure of 6 kg/cm^2, an SV of 1 hr^{-1} and an H_2/oil ratio of 1000 and the results are shown in Fig.4.

As can be seen from Tables 3-5 and Fig.4, cracking rate reached 50% or higher in the case of catalysts A-E. With increase of reaction temperature and pressure, aromatic components increased. Aromatic components are apt to reduce activity of catalyst due to deposition of carbon on catalyst. So, production of aromatic components must be lowered.

Y-type zeolite, Mo-silicate, W-silicate, Cr-silicate and Ga-silicate catalysts also showed the cracking activity for kerosene similar to that of catalyst B.

As explained above, according to the present invention, cracking and desulfurizing catalysts having a cracking rate of 50% or higher for kerosene and naphtha have been able to be developed.

When kerosene (sulfur content 25 ppm) was used as raw material oil and cracking was conducted using catalyst A at a reaction temperature of 500°C, fractions of C_9 and lower in the product reached 60% or higher with sulfur content of less than 0.1 ppm, and fractions of C_{12} and lower reached 85%. Amount of aromatics produced was small.

Claims

1. A method for producing raw materials for a r former by cracking and desulfurizing petroleum fuels in a desulfuriz r, in a fuel cell electricity generation process, which comprises cracking and desulfurizing the petroleum fuel at a temperature of 300-600°C, a pressure of 1-10 kg/cm^2, an H_2/oil ratio of 500-2000, and an SV of 0.5-4 hr^{-1}, using a zeolite catalyst or a metallosilicate catalyst as desulfurizing catalyst.

2. A method according to claim 1, wherein the lectricity gen ration process f fuel cell compris s a desulfurizer, an adsorber, a reformer, a converter or gas separation membrane, and a cell.

3. A method according to claim 1, wherein the zeolite catalyst is Y-type zeolite.

4. A method according to claim 1, wherein the metallosilicate catalyst has an atomic ratio Si/Me of 40-3200 wherein Me is a metal selected from the group consisting of Al, Ni, Co, Mo, W, Fe, Cr and Ga.

5. A method according to claim 1, wherein the petroleum fuel is kerosene, naphtha or LPG.

6. A method according to claim 1, wherein the raw material which is fed to the reformer has a specific gravity of 0.5-0.85 and comprises C_3-C_{20} hydrocarbons.

7. A method according to claim 1, wherein conditions in the reformer are a temperature of 700-800°C, a pressure of at most 10 kg/cm^2, a molar ratio H_2O/C of at least 2, and an SV of 0.5-4.0 hr^{-1}.

8. A method according to claim 7, wherein gas produced in the reformer comprises 65-80 vol% of H_2, 5-20 vol% of CO, and 5-25 vol% of CO_2.

9. A method according to claim 1, wherein in the converter a high-temperature shift reaction or a low-temperature shift reaction is carried out.

10. A method according to claim 1, wherein in the converter a high-temperature shift reaction and low-temperature shift reaction are carried out.

11. A method according to claim 1, wherein the gas separation membrane comprises polyimide.

12. A method according to claim 1, wherein when the gas separation membrane is used, the reformed gas is treated at 50-150°C and under a pressure of 2-10 kg/cm^2.

FIG. 1

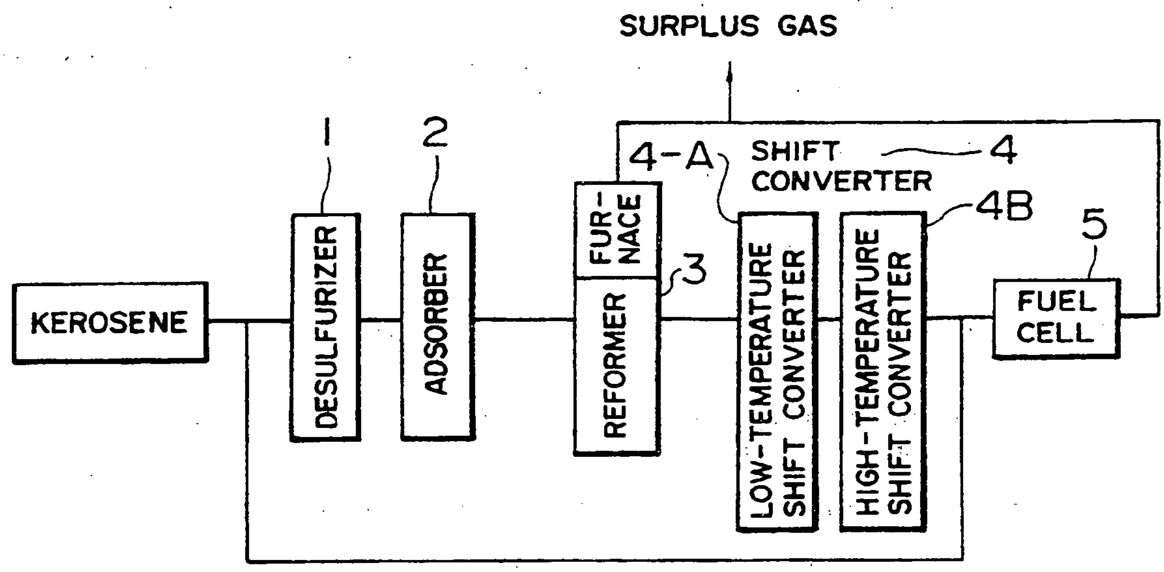

SURPLUS GAS
1
2
4-A
SHIFT CONVERTER
4
4B
5
FUR-NACE
3
KEROSENE
DESULFURIZER
ADSORBER
REFORMER
LOW-TEMPERATURE SHIFT CONVERTER
HIGH-TEMPERATURE SHIFT CONVERTER
FUEL CELL

FIG. 2

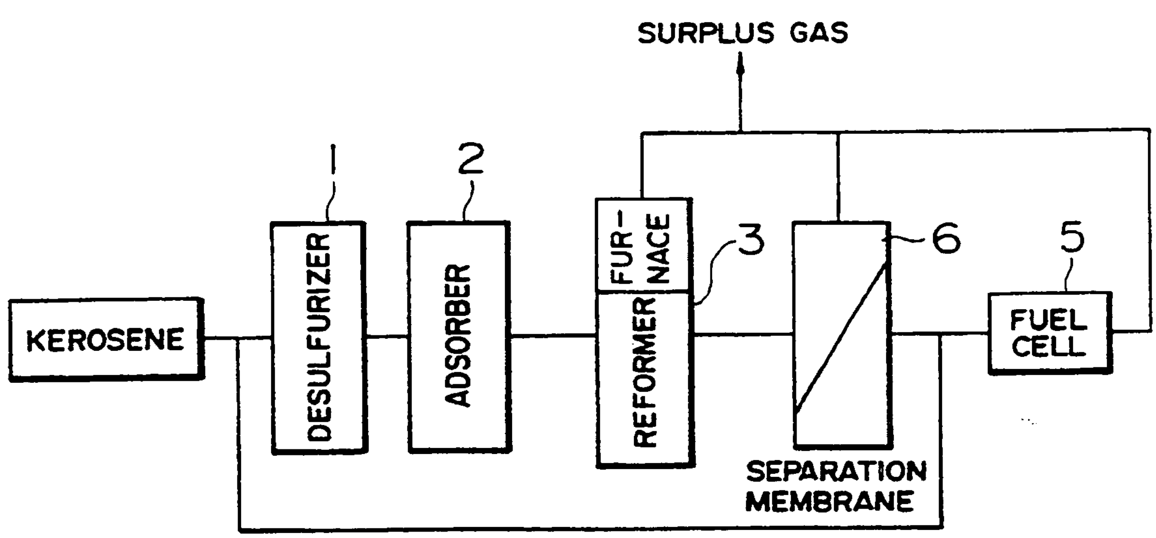

SURPLUS GAS
1
2
FUR-NACE
3
6
5
KEROSENE
DESULFURIZER
ADSORBER
REFORMER
FUEL CELL
SEPARATION MEMBRANE

FIG. 3

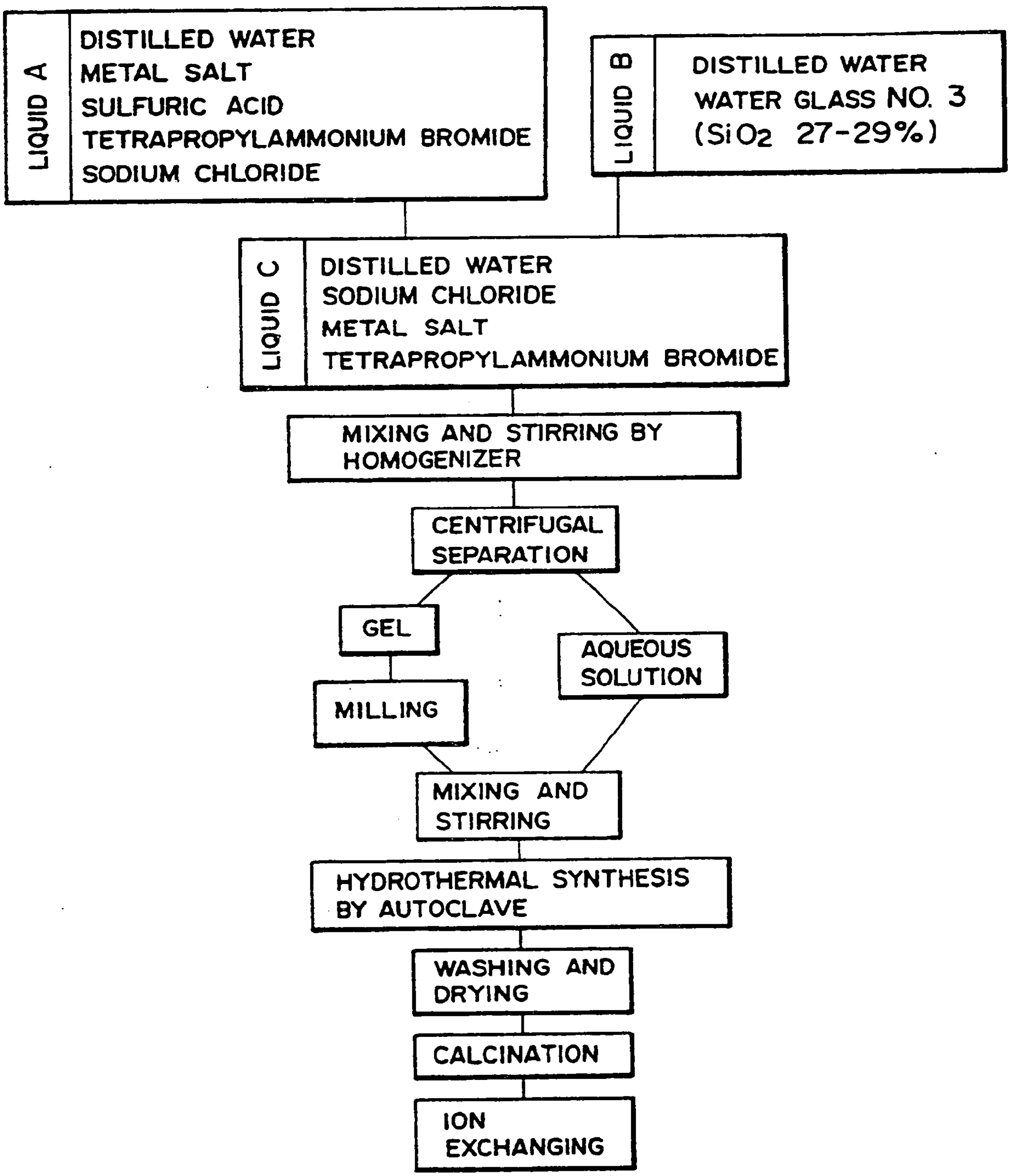
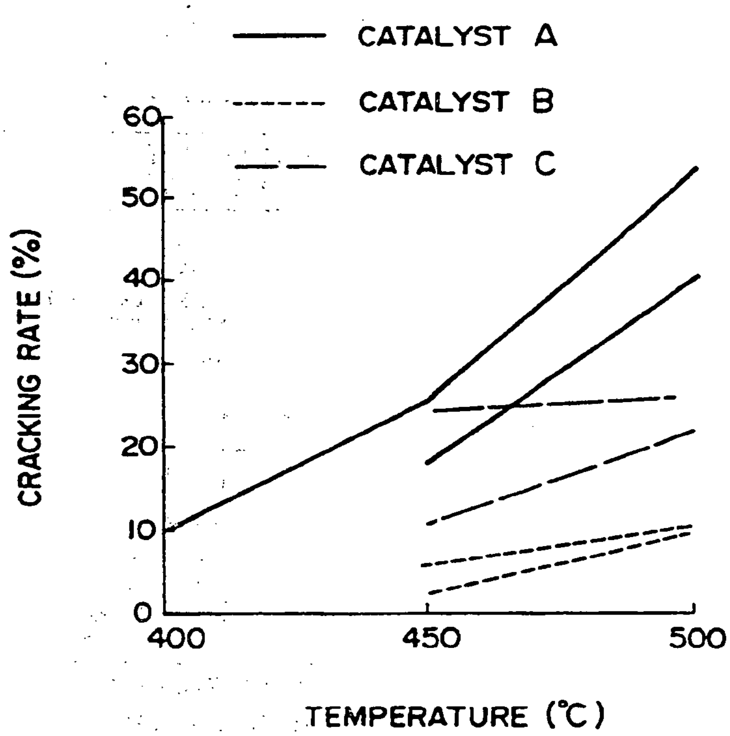

LIQUID A
DISTILLED WATER
METAL SALT
SULFURIC ACID
TETRAPROPYLAMMONIUM BROMIDE
SODIUM CHLORIDE
LIQUID B
DISTILLED WATER
WATER GLASS NO. 3
(SiO_2 27-29%)
LIQUID C
DISTILLED WATER
SODIUM CHLORIDE
METAL SALT
TETRAPROPYLAMMONIUM BROMIDE
MIXING AND STIRRING BY HOMOGENIZER
CENTRIFUGAL SEPARATION
GEL
AQUEOUS SOLUTION
MILLING
MIXING AND STIRRING
HYDROTHERMAL SYNTHESIS BY AUTOCLAVE
WASHING AND DRYING
CALCINATION
ION EXCHANGING

FIG. 4


CATALYST A
CATALYST B
CATALYST C
CRACKING RATE (%)
0
10
20
30
40
50
60
400
450
500
TEMPERATURE (℃)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90403643.1

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US - A - 4 816 353 (WERTHEIM et al.) * Abstract; column 7, lines 14-34 * --	1,2	H 01 M 8/06 C 10 G 45/00
A	CHEMICAL ABSTRACTS, vol. 105, no. 26, December 29, 1986, Columbus, Ohio, USA SATO, KAZUO et al. "Desulfurization apparatus" page 190, abstract-No. 229 974e & Jpn. Kokai Tokkyo Koho JP 61 163 568 --	1,2	
A	US - A - 4 151 119 (GLADROW) * Claims 1,4 * --	3,4	
A	US - A - 4 336 130 (MILLER et al.) * Abstract; claim 1 * ----	4,5	TECHNICAL FIELDS SEARCHED (Int. Cl.5) H 01 M C 10 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	18-02-1991	LUX

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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